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Chemical Modification of Poly(p-Phenylene) for Use in Ablative Compositions

The problem:

Determine whether p-phenylene polymers can be structurally altered to limit spalling under high temperature, high heat flux conditions. Polyphenylenes offer significant advantages as ablative materials because their skeletal structures consist of long chains of conjugated aromatic rings which, on thermal or radiative degradation, produce a maximum amount of char, in the form of a thermally resistant graphitic structure, and yield a minimum amount of gaseous products other than hydrogen. However, the integrity of molded ablative composites containing poly(p-phenylene) is destroyed by spalling (or by exfoliation) when the composites are exposed to the high temperatures and heat fluxes of an oxyacetylene torch.

The solution:

Incorporate chlorine into the polymeric structure. This produces potential cross-linking sites for subsequent pyrolysis, increases the char yield, and increases the physical integrity of the composite's char layer.

The chemical and physical properties of the chlorinated polyphenylene composites suggest possible applications as brake lining material and thermal insulation at high temperatures.

How it's done:

In the synthesis of linear polyphenylenes, a small amount (less than 1%) of chlorine was incorporated in the polymer. The chlorine was derived from the catalysts, cupric and aluminum chlorides. When benzene was polymerized in the presence of these two catalysts, at temperatures below 35° C and reaction times of less than two hours, a usual reaction product contained about 0.8% chlorine, a carbon-to-hydrogen ratio of

about 1.50, and no detectable ortho, meta, or nonaromatic linkages. Reaction conditions were established to produce polymers which contained higher chlorine contents and appeared to be polynuclear ring structures. The polymers containing 4 to 6% chlorine had significantly improved ablation characteristics.

The increased chlorine content of the polymers was achieved by two different methods; i.e., direct and post-halogenation techniques. Direct halogenation was accomplished by the incremental addition of catalyst at the reflux temperature of benzene during the polymerization reaction. The post-halogenation was accomplished by bubbling chlorine gas into a suspension of the linear polymer in the presence of a ferric chloride catalyst.

Polyphenylenes containing chlorine and polynuclear structures pyrolyze in two distinct stages; essentially all of the chlorine content is lost in the first stage; and degradation products, which are markedly deficient in aromatic pyrolyates, are formed in the second stage (which is apparently the same as that of unchlorinated polymers).

Thermogravimetric and gas chromatographic analyses showed that the "unchlorinated" polymer degrades by chain scission, with multiples of phenyl units given off after an initial loss of hydrogen and methane at the lower temperatures. Chain scission was decreased mainly through nuclear condensation and "thermal" cross-linking at the higher temperatures, above 550° C, so that a good char yield of 82% was obtained in an inert atmosphere to temperatures of 900° C. In contrast, the chlorinated polymer underwent little chain scission, so that the char yield was even greater, 88%. This can be explained by dehydrohalogenation, taking place at temperatures below about

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550° C, effecting chemical cross-linking and nuclear condensation at the earlier stages of pyrolysis. Most of the weight loss of the chlorinated polymer in the first stage of pyrolysis was due to the loss of chlorine (as HCl). If the elimination of HCl is made to occur in a "curing" step, char yields of up to 94% could be obtained from the cured polymer, based on calculations of carbon retention alone.

The incorporation of small amounts (4 to 12 parts per hundred) of chopped quartz or carbon fiber prevents the cracking of heavy sections during the curing step; poor adhesion between the polymer and the fibrous filler imparts sufficient porosity to allow the escape of gaseous products generated during the curing process. One inch diameter samples, containing chlorinated polyphenylene mixed with chopped quartz or carbon fiber and cured at 550° C for 30 minutes, were exposed for 20 minutes to an oxyacetylene flame under conditions of 3.95 watt/meter² (350 BTU/ft²sec) heat flux and 2000°C surface temperature. A hard, tightly adherent char layer was formed to a depth of about 0.5 cm, with a surface regression of less than 0.25 cm. In contrast, uncured samples or samples containing unchlorinated polyphenylene spalled severely.

Notes:

1. When the improved composite is exposed to the oxyacetylene flame, large sections may fail due to thermal stresses; small samples maintain their integrity.
2. Requests for further information may be directed to:

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No patent action is contemplated by NASA.

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